MTL TR 92-38

(2)

SITE COMPETITION OF IMPURITIES AND GRAIN BOUNDARY STABILITY IN IRON

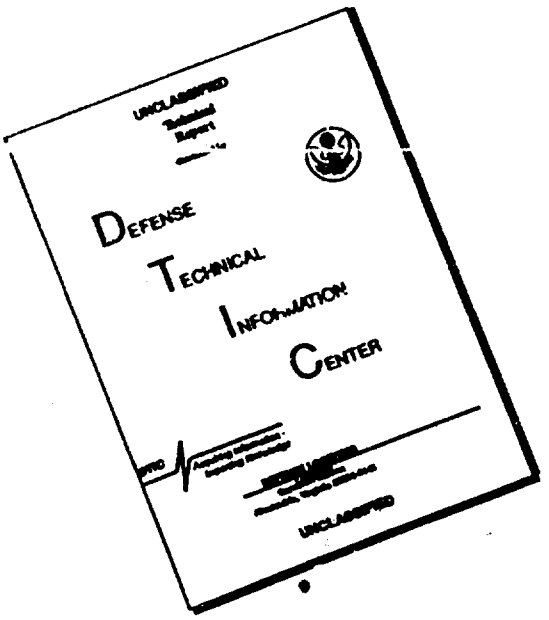
GENRICH L. KRASKO
METALS RESEARCH BRANCH

June 1992

US ARMY
LABORATORY COMMAND
MATERIALS TECHNOLOGY LABORATORY

U.S. ARMY MATERIALS TECHNOLOGY LABORATORY
Watertown, Massachusetts 02172-0001

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Mention of any trade names or manufacturers in this report shall not be construed as advertising nor as an official indorsement or approval of such products or companies by the United States Government.

DISPOSITION INSTRUCTIONS

Destroy this report when it is no longer needed.
Do not return it to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER MTL TR 92-38	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* SITE COMPETITION OF IMPURITIES AND GRAIN BOUNDARY STABILITY IN IRON		5. TYPE OF REPORT & PERIOD COVERED Final Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR*(s)* Genrich L. Krasko		8. CONTRACT OR GRANT NUMBER*(s)*
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Materials Technology Laboratory Watertown, Massachusetts 02172-0001 SLCMT-EMM		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Laboratory Command 2800 Powder Mill Road Adelphi, Maryland 20783-1145		12. REPORT DATE June 1992 13. NUMBER OF PAGES 10
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

Presented at 1992 MRS fall meeting, Boston, MA, November 1991

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Site competition
Grain boundaries
Iron
Impurities
Relaxation

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

(SEE REVERSE SIDE)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

Block No. 20

ABSTRACT

Impurities such as H, P, S, B, etc., have a very low solubility in iron and, therefore, prefer to segregate at the grain boundaries (GBs). In order to analyze the energetics of impurities on the iron GB, the Linear Muffin Tin Orbitals (LMTO) calculations were performed on a simple 8-atom supercell emulating a typical (capped trigonal prism) GB environment. The so-called *environment-sensitive* embedding energies (EE) were calculated for H, B, C, N, O, Al, Si, P, and S as a function of the electron charge density due to the host atoms at the impurity site. It was shown that, at the electron charge density typical of a GB, B and C have the lowest energy among the analyzed impurities and, thus, would compete with them for the site on the GB tending to push the other impurities off the GB. The above energies were then used in a modified Finnis-Sinclair embedded atom approach for calculating the equilibrium interplanar distances in the vicinity of a (111) Σ3 tilt GB plane, both for the clean GB and that with an impurity. These distances were found to be oscillating, returning to the equilibrium spacing between (111) planes in bulk BCC iron by the 10th to 12th plane off the GB plane. H, B, C, N, and O actually dampen the deformation wave (making the oscillation amplitudes less than in the clean GB) while Al, Si, P, and S result in an increase of the oscillations. The effect of B, C, N, and O may be interpreted as cohesion enhancement; this conclusion supports our earlier first-principles results on B and C.

INTRODUCTION

The reduced cohesion of grain boundaries (GBs) is known to be often the controlling factor limiting ductility and, actually, the performance and reliability of high-strength metallic alloys.[1] Intergranular embrittlement in metals is usually caused by impurities segregating towards the GBs.[2-5] Impurities present in bulk concentrations of 10^{-3} to 10^{-4} atomic percent can result in a dramatic decrease of plasticity, drastically degrading mechanical properties of metallic alloys and thus posing significant technological problems. This detrimental effect of just ppm of impurities may be readily understood: a simple estimate shows that a ppm amount of impurity is sufficient for saturating all the grain boundaries in a typical grain-size polycrystal.

Recent progress in developing efficient methods of first-principles calculations and computational algorithms made possible systematic studies of the role of impurities in intergranular cohesion on the electron-ion level. Calculations on both cluster,[6] two-dimensional,[7,8] and supercell[9,10] models of GBs with impurities have provided an in-depth insight into mechanisms of GB decohesion.

Since the first-principles electronic calculations on low-symmetry systems (such as lattice defects or GBs) are still extremely complicated and expensive, semi-empirical methods based upon solid first-principles foundations have been developed; among them, the most popular is the Embedded Atom Method (EAM).[11-13] This method has been successfully used in a wide variety of calculations.

The purpose of this report is to elucidate energetics of impurities on an iron GB and analyze the effect of impurities on the intergranular cohesion in iron.

Rather than doing sophisticated first-principles calculations on multi-atom models of a GB, it was decided to calculate the quantity which may be called *environment-sensitive* embedding energy (EE), the energy of an impurity atom in an atomic environment typical for a GB (capped trigonal prism). Knowledge of these energies for different impurities enables one to compare the relative stability of a particular impurity in the iron GB. The approach taken is obviously an extension of the so-called *Effective Medium* (EM) theory.[14-19]

Having calculated the EEs for a number of impurity atoms, one can use this information on the impurity energetics in a modified EAM approach for calculating the GB relaxation. The latter calculations enables one to draw important conclusions regarding the intergranular cohesion in iron in the presence of a definite impurity in the GB.

RESULTS AND DISCUSSION

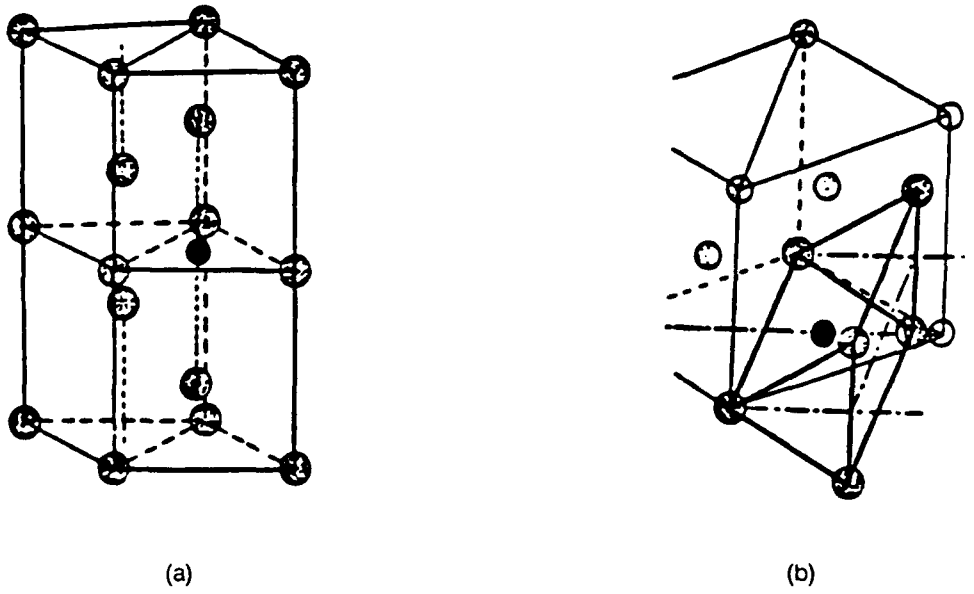
Environment Sensitive Embedding Energies

The basic idea of the EM approach was to replace the low symmetry system consisting of an atom plus a host matrix by a high symmetry effective system of the atom and the homogeneous electron gas of a density equal to that seen by the atom. The energy of interest was called the embedding energy and was equal to the energy difference between the atom embedded in the electron gas and, separately, the isolated atom and the electron gas.

The EM theory, as a first and very crude approximation, completely neglected any covalent effects, though one could expect that a metalloid impurity in a transition metal would develop strong sp-d hybridization resulting in covalent bonds. The introduction of covalent effects via perturbation theory,[18] resulted in significant corrections in the embedding function for hydrogen. Further attempts to improve upon the EM method were undertaken in recent years.[20]

Improvements in the EM theory actually made calculations more sophisticated, spoiling the elegant simplicity of the original method. Rather than introducing corrections to the EM concept, it was decided to perform first-principles calculations on a simplified model of a GB environment, varying hydrostatically all the characteristic volumes, thus generating a series of *environment sensitive* EEs as a function of the electron charge density due to the host (iron) atom at the impurity site. In this case an impurity is actually *embedded* into a crystal lattice environment rather than into an electron jellium as in the original EM theory.

The model chosen for the GB environment is an 8-atom hexagonal supercell (Fe_6X, where X is an impurity atom). The supercell is shown in Figure 1 together with the capped trigonal prism coordination of the surrounding iron atoms.



(a) (b)

Figure 1. The Fe_6X hexagonal supercell emulating a typical trigonal prism environment of iron atoms in the (111) Σ3 GB: a) the supercell; b) the trigonal prism coordination; ⊙ Fe, ● Impurity.

A trigonal prism GB configuration follows from the theory of hard-sphere packing.[21] Atomistic relaxation studies have also shown[22] that an impurity atom such as P or B is likely to occupy an interstitial position in the center of the trigonal prism formed by iron atoms in the GB core (even if, as in the case of P and B, the impurity forms a substitutional solid solution with the host). The hexagonal supercell has been chosen both because of its relatively high symmetry and its emulation of a (111) Σ3 GB environment.[9,10]

The spin-polarized scalar-relativistic Linear Muffin Tin Orbitals (LMTO)[23] calculations were performed; the von Barth-Hedin[24] exchange-correlation and the frozen core

approximations were also used. First, a series of calculations (for six different volumes) was performed with an impurity absent from the supercell; i.e., an empty sphere of the same radius as that of the radius of the impurity's Wigner-Seitz sphere was substituted for the latter. Similar calculations were then performed for each of the impurities: H, B, C, N, O, Al, Si, P, and S. The EEs were defined as follows:

$$EE = E(Fe_6\bullet)-E(Fe_6O)-E(\bullet) \quad (1)$$

where $E(Fe_6\bullet)$ and $E(Fe_6O)$ are, respectively, the energies of the supercell with and without the impurity (O stands for an empty sphere substituted for the impurity atom), and $E(\bullet)$ is the energy of the free impurity atom. In order to make the calculations more consistent, the values of $E(Fe_6\bullet)-E(Fe_6O)$ extrapolated to the zero charge density (n = O), were chosen to be used as $E(\bullet)$s which would correspond to the energies of impurities in the GB environment with the host crystal lattice infinitely expanded. The EE energies (see Equation 1) as a function of n, the electron charge density due to iron atoms at the impurity site, are presented in Figure 2.

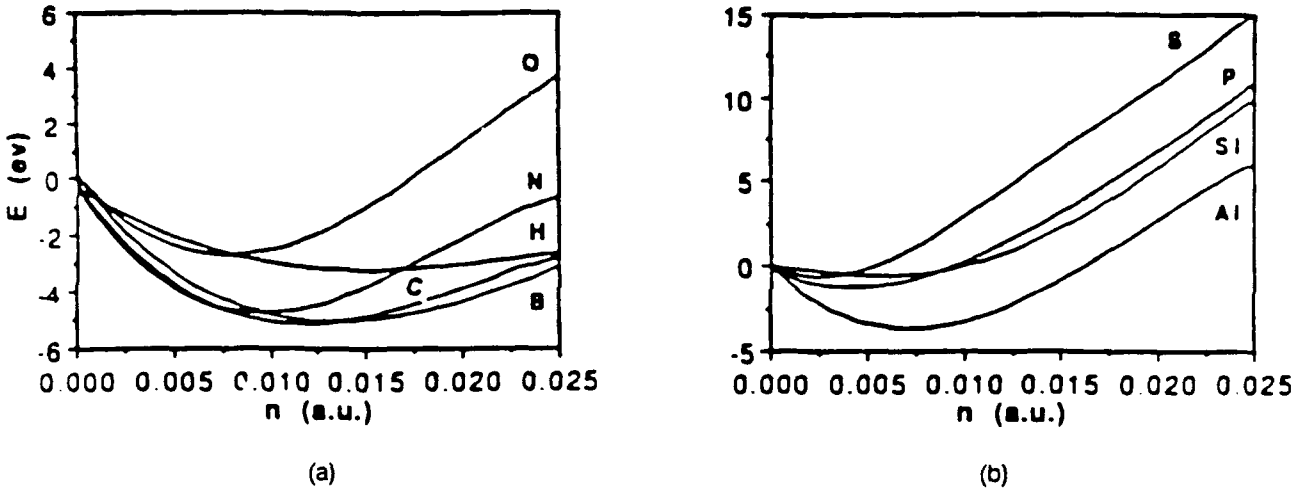


Figure 2. The *environment sensitive* EEs versus electron charge density (in atomic units, a.u.). a) Hydrogen and impurities of the second period; b) Impurities of the third period.

Plots in Figure 2 explain an experimentally observed phenomenon known as *site competition.* As can be seen, in the range of electron charge density typical of a GB (0.015 a.u. to 0.025 a.u.), B and C have the lowest energies and, thus, would push the other impurities off the GB. In fact, C is known to successfully compete with P[25] and S,[26,27] and N -- with P[28] and S.[26] B should even be more efficient in pushing the harmful impurities off the GB, though the energy difference between B and C is not very significant. Since, in principle, EEs are to be sensitive to the type and orientation of the GB, in some GBs B and C may compete in a reverse way. Also, it can be seen that H would successfully compete with all the impurities but B and C; N being a marginal case.

The plots in Figure 2 also reveal an important aspect of GB impurity behavior. All the plots (except for H) have well pronounced minima. The positions of the minima correspond to electron density at the impurity site due to the surrounding Fe atoms which would occur if the GB were allowed to relax in such a way as to minimize the impurity's energy. The

minima positions systematically shift towards lower densities with the impurity loosing its competitive power. Lower charge density means a more *loose* GB, less strong and more prone to decohesion. The minimization of the total GB energy (not only the energy of the impurity atom) gives the characteristic charge densities which are somewhat higher than those in the minima. However, from this point of view, only S, P, Si, and Al are the obvious candidates for being *decohesive*, O and N are marginal, while B, C, and H may be called *cohesion enhancers* (the behavior of H will be discussed in more detail below). Calculations of GB relaxation shed more light on intergranular cohesion/decohesion due to impurities.

Grain Boundary Relaxation

First-principles calculations are still too expensive to be used for the investigation of GB relaxation. A semi-empirical EAM is obviously more appropriate. In order to find both embedding functions and pair potentials, the EAM uses experimental data such as cohesive energies and elastic moduli for the system of interest. This approach is easily applicable to pure metals and compounds but may become, in fact, inappropriate if the effect of an isolated impurity atom or an impurity atom on a GB is to be studied. For example, in principle one can, in a metal-hydrogen system, use the embedding function and the pair potentials found from experimental information on that metal's hydrides. This information, however, can be misleading since the effect of isolated hydrogen atoms on electronic structure and cohesive properties of the metal may be completely different from that of periodic arrays of hydrogen atoms typical of hydrides. Krasko and Olson[10] found that hydrogen in the iron GB does not contribute its electron to the iron d-valence band at all, contrary to a general belief that in transition metals the hydrogen's electron will inevitably go to a d-band.

In order to resolve this difficulty the energy contributions due to impurity atoms in the GB were calculated by using the EEs discussed above. Since the EAM functions are also fundamentally dependent upon the electron charge density at an atom site, the EEs may simply be added to the EAM energy of the host atoms:

$$E = \Sigma_R\, E_{emb}(n(R)) + 1/2\Sigma_{R,R'}\, V(R,R') + EE(n(R_{imp})) \qquad (2)$$

where E_{emb} (n) and $V(R,R')$ are the EAM embedding energy and the pair potential as found for the bulk BCC Fe (the Finnis-Sinclair functions and parameters[12] were used). The third term is the energy of the impurity atom. R and R′ are the positions of the host atoms, R_{imp} is that of the impurity, and $n(R)$ and $n(R_{imp})$ are the electron charge densities at the site of a host atom and the impurity, respectively. The electron charge density at a given site can be taken to be a superposition of the free atom charge densities or found from more sophisticated procedures.

As mentioned above, the GB environment dealt with was that of the (111) Σ3 tilt GB. The GB structure can be represented as a succession of (111) hexagonal planes:

....CBACBACBACBACBABCABCABCABCABC....

(the GB plane is marked by A). The CBABC atomic structure of the core of the GB (clean or with an impurity) was just emulated by the supercell and shown in Figure 1. In order to find the GB structure corresponding to a minimum of energy, (see Equation 2) the inter-

planar distances were varied while the interatomic spacings and the structure within the (111) planes were unchanged.

Figure 3 shows the set of plots of *relaxed* interplanar distances for the GBs with different impurities as a function of the plane number, i. It can be seen that the interplanar distances oscillate; the deformation waves decaying by the 10th to 12th plane off the GB.

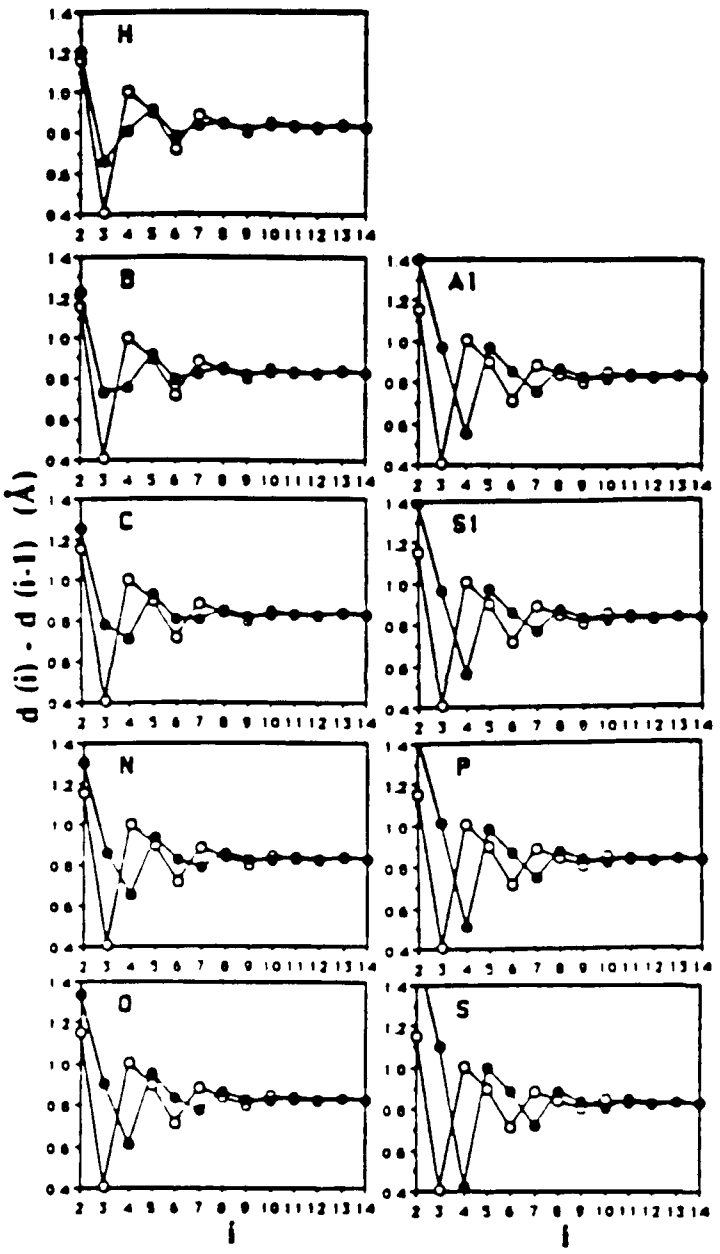


Figure 3. *Relaxed* distances between GB planes number i and i-1: O clean GB, • GB with impurity (i = 1 corresponds to the GB plane A).

An interesting feature of the clean GB relaxation is that the distance between the second and third planes is only half of the (111) interplanar distance in bulk BCC Fe (0.407 Å versus 0.825 Å). The LMTO calculations[29] show that it is only the interaction between Fe atoms in planes 3, 4, 5, and 6 that prevents plane 3 from collapsing into plane 2 (the ω-phase configuration). The site-projected electronic densities of states of the Fe atoms in planes 1 through 3 are very similar to that typical of an ω-phase.[10]

The impurity atoms, H, B, C, N, and O result in some *damping* of the relaxation deformation waves; i.e., decreasing the oscillation amplitudes. This damping is most pronounced for H, B, and C while N and O are marginal. The amplitude increases with Al, Si, P, and S. Damping the deformation wave may be interpreted as *cohesion enhancement* while increasing the deformation wave oscillations may be thought of as resulting in *decohesion*.

C and N are known to be GB cohesion enhancers in steels;[25-28] O, Si, P, and S, being strong embrittlers, are believed to weaken the GB cohesion.[30] The results agree with both this experimental information and the earlier first-principles calculations[9] on B, C, P, and S.

H is one of the worst embrittlers of steels. At the same time, the first-principles calculations[10] do not show any dramatic GB decohesion due to H. In fact, H is quite *neutral*; a weak H-Fe covalent bond does not significantly disturb the GB energetics, and the H electron does not participate in metallic bonding. Also, the calculations of both the EE and the GB relaxation do not show any sign that the presence of H in the GB should weaken it dramatically. However, the EAM calculation[13] has shown that a H atom on a Ni GB does weaken the metallic bond across the GB, lowering the fracture stress by some 15%.

From a thermodynamic point of view,[31] the impurity's embrittling potency depends upon the difference between the free energies of the impurity's segregation on the initial GB and on the two free surfaces emerging upon fracture. The higher the difference, the stronger the embrittling potency of the impurity. As a less rigorous but simpler criterion, in Reference 30 the sublimination energy differences between the host and impurity were calculated in an ideal solution model for over 60 elements. The effects of impurities on GB stability can be analyzed by simply comparing the GB energy differences between the GB with impurities and the clean GB.

The corresponding values for the impurities discussed are plotted in Figure 4. It is noted that the ΔE values are negative for impurities that can be thought of as *cohesion enhancers*, and positive for the *embrittlers*. O and Al, the *marginal* impurities, have low negative values. The ΔE for H is also slightly negative.

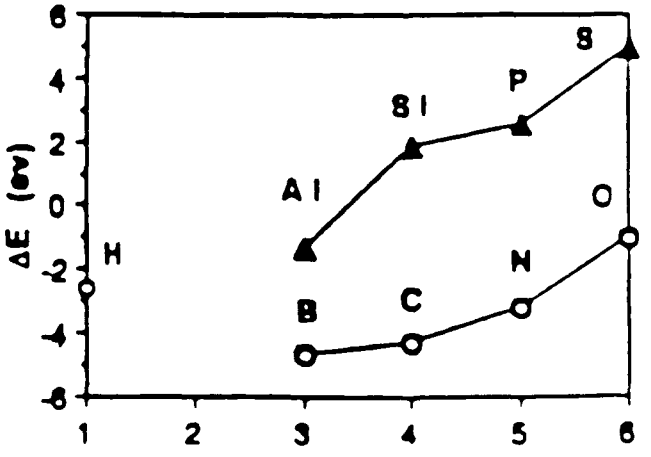


Figure 4. $\Delta E = E_{GB}(X)-E_{GB}(cln)$, the energy difference between the GB with impurity X and clean GB, versus the Periodic Chart group number.

CONCLUSIONS

The *environment sensitive* EEs (the energies of an impurity atom in an environment typical of a GB in Fe as a function of electron charge density at the impurity site) were calculated for a number of impurities often present in Fe and Fe-base alloys. The knowledge of these energies enabled us to explain the well known site competition effect and draw important conclusions about the relative stability of GBs with different impurities. The calculation of GB relaxation also revealed some interesting features of the GB. The impurities known as cohesion enhancers tend to suppress the deformation wave oscillations while the embrittling impurities increase the oscillations. The detrimental effect of hydrogen in steels cannot be explained from the knowledge of its *static* energetics. In order to explain hydrogen's extreme embrittling potency, one should probably investigate the dynamics of hydrogen atoms in the GB vicinity. Since the EEs may be easily calculated for various host environments, a modified EAM may be used to analyze the impurity's energetics in a variety of situations.

ACKNOWLEDGMENTS

This research is a part of the multi-institutional Steel Research Group (SRG) program. Discussions with Professor G. B. Olson, Professor J. C. Rice, and Dr. J. S. Wang are gratefully acknowledged. The author is also grateful to Dr. R. P. I. Adler and Dr. M. Azrin of MTL for their interest and invaluable support. The LMTO code used in calculations was developed by Professor N. Christensen.

REFERENCES

1. BRIANT, C. L., and BANERJI, S. K. *Embrittlement of Engineering Alloys*. C. L. Briant and S. K. Banerji, eds., Academic Press, New York, NY, 1983, p. 21; GUTTMANN, M., and MCLEAN, D. *Interfacial Segregations*. W. C. Johnson and J. M. Blakely, eds., ASM, Metals Park, OH, 1979, p. 261.
2. TROIANO, A. R. Trans. Am. Soc. Met., v. 52, 1960, p. 54.
3. STARK, J. P., and MARCUS, H. L. Metall. Trans. A., v. 8A, 1977, p. 1423; LEE, D. Y., BARRERA, E. V., STARK, J. P., and MARCUS, H. L. Metall. Trans. A., v. 15A, 1984, p. 1415.
4. MEYERS, C. L., Jr., ONODA, G. Y., LEVY, A. V., and KOTFILA, R. J. Trans. Metall. Society of AIME, v. 233, 1965, p. 720.
5. SEAH, M. P. J. Phys. F., v. 10, 1980, p. 1043.
6. EBERHART, M. E., JOHNSON, K. H., and LATANISION, R. M. Acta Metall., v. 32, 1984; p. 955; EBERHART, M. E., LATANISION, R. M., and JOHNSON, K. H. *ibid*, v. 33, 1985, p. 1769; EBERHART, M. E., and VVEDNESKY, D. D. *Chemistry and Physics of Fracture*, R. H. Jones and R. M. Latanision, eds., Martinus Nijhoff, 1987, p. 163.
7. HASHIMOTO, M., ISHIDA, Y., YAMAMOTO, R., DOYAMA, M., and FUJIWARA, T. J. Phys. F, v. 11, 1981, p. L141; Surface Sci., v. 144, 1984, p. 182; HASHIMOTO, M., ISHIDA, Y., WAKAYAMA, S., YAMAMOTO, R., DOYAMA, M., and FUJIWARA, T. Acta Metall., v. 32, 1984, p. 13.
8. CRAMPIN, S., VVEDENSKY, D. D., MACLAREN, J. M., and EBERHART, M. E. Phys. Rev., v. B40, 1989, p. 3413.
9. KRASKO, G. L., and OLSON, G. B. Solid State Commun., v. 76, 1990, p. 247.
10. KRASKO, G. L., and OLSON, G. B. Solid State Commun., v. 79, 1991, p. 113.
11. DAW, M. S. Phys. Rev., v. B39, 1989, p. 7441; DAW, M. S., and BASKES, M. I. *ibid*, v. B29, 1984, p. 6443.
12. FINNIS, M. W., and SINCLAIR, J. E. Phil. Mag., v. A50, 1984, p. 45; v. A53, 1986, p. 161.
13. DAW, M. S., and BASKES, M. I. Phys. Rev. Lett., v. 50, 1983, p. 1285; DAW, M. S., and BASKES, M. I. *Chemistry and Physics of Fracture*, R. H. Jones and R. M. Latanision, eds., Martinus Nijhoff, 1987, p. 196.
14. NØRSKOV, J. K., and LANG, N. D. Phys. Rev., v. B21, 1980, p. 2136.
15. STOTT, M. J., and ZAREMBA, D. M. Phys. Rev., v. B22, 1980, p. 1564.
16. PUSKA, M. J., NIEMINEN, R. M., and MANNINEN, M. Phys. Rev., v. B24, 1981, p. 3037.
17. STOTT, M. J., and ZAREMBA, E. Can. J. Phys., v. 60, 1982, p. 1145.
18. NØRSKOV, J. K. Phys. Rev., v. B26, 1982, p. 2875.
19. JACOBSEN, K. W., NØRSKOV, J. K., and PUSKA, M. J. Phys. Rev., v. B35, 1987, p. 7423.
20. RAEKER, T. J., and DEPRISTO, A. E. Surface Sci., v. 235, 1990, p. 84; and references therein.
21. ASHBY, M. F., SPAEPEN, F., and WILLIAMS, S. Acta Metall., v. 26, 1978, p. 1647; ASHBY, M. F., and SPAEPEN, F. Scripta Met., v. 12, 1978, p. 193; FROST, H. F., ASHBY, M. F., and SPAEPEN, F. Scripta Met., v. 14, 1980, p. 1051.
22. HASHIMOTO, M., ISHIDA, Y., YAMAMOTO, R., DOYAMA, M., and FUJIWARA, T. Scripta Met., v. 16, 1982, p. 267; HASHIMOTO, M., ISHIDA, Y., YAMAMOTO, R., and DOYAMA, M. Acta Metall., v. 32, 1984, p. 1; ISHIDA, Y., and MORI, M. Journal de Physique, Colloque, C4, v. 46, 1985, p. C4-465.
23. ANDERSEN, O. K., JEPSEN, O., and GLÖTZEL. *Highlights of Condensed Matter Theory*. F. Bassani, F. Fumi, and M. P. Tosi, eds., North Holland, NY 1985; ANDERSEN, O. K. *Electronic Structure of Complex Systems*, P. Phariseau and W. M. Timmerman, eds., Plenum Press, New York, NY, 1984, p. 11; SKRIVER, H. L. *The LMTO Method*. Springer, Berlin, 1984.
24. von BARTH, U., and HEDIN, L. J. Phys., v. C5, 1972, p. 1629.
25. MÖLLER, R., HÄNSEL, H., and GRABKE, H. J. Scr. Metall., v. 18, 1984, p. 527; GRABKE, H. J. Scr. Metall., v. 20, 1986, p. 1641; SUZUKI, S., OBATA, M., ABIKO, K., and KIMURA, H. Trans. Iron Steel Inst. Jpn., v. 25, 1985, p. 62.
26. TAUBER, G., and GRABKE, H. J. Ber. Bunsenges Phys. Chem., v. 82, 1978, p. 198.
27. SUZUKI, S., TANII, S., ABIKO, K., and KIMURA, H. Metall. Trans., v. A18, 1987, p. 1109; GRABKE, H. J. Steel Research, v. 57, 1986, p. 178; SHIN, K. S., and TSAO, B. H. Scr. Metall., v. 22, 1988, p. 585.
28. ERHART, H., and GRABKE, H. J. Scr. Metall., v. 15, 1981, p. 531.
29. KRASKO, G. L. Unpublished
30. SEAH, M. P. Acta Metal., v. 28, 1980, p. 955.
31. RICE, J. C. *Effect of Hydrogen on Behavior of Materials*. A. W. Thomson, and I. M. Bernstein, eds., The Metallurgical Society of AIME, Warrendale, PA, 1976, p. 455; HIRTH, J. P., and RICE, J. R. Metall. Trans., v. A11, 1980, p. 1502; RICE, J. R., and WANG, J.-S. Mat. Sci. and Eng. A, v. 107, 1989, p. 23.

DISTRIBUTION LIST

No. of Copies	To
1	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301
	Commander, U.S. Army Laboratory Command, 2800 Powder Mill Road, Adelphi, MD 20783-1145
1	ATTN: AMSLC-IM-TL
1	AMSLC-CT
	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 22304-6145
2	ATTN: DTIC-FDAC
1	MIAC/CINDAS, Purdue University, 2595 Yeager Road, West Lafayette, IN 47905
	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211
1	ATTN: Information Processing Office
	Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333
1	ATTN: AMCSCI
	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005
1	ATTN: AMXSY-MP, H. Cohen
	Commander, U.S. Army Missile Command, Redstone Scientific Information Center, Redstone Arsenal, AL 35898-5241
1	ATTN: AMSMI-RD-CS-R/Doc
1	AMSMI-RLM
	Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801
1	ATTN: Technical Library
	Commander, U.S. Army Natick Research, Development and Engineering Center, Natick, MA 01760-5010
1	ATTN: Technical Library
	Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703
1	ATTN: Technical Document Center
	Commander, U.S. Army Tank-Automotive Command, Warren, MI 48397-5000
1	ATTN: AMSTA-ZSK
1	AMSTA-TSL, Technical Library
	Commander, White Sands Missile Range, NM 88002
1	ATTN: STEWS-WS-VT
	President, Airborne, Electronics and Special Warfare Board, Fort Bragg, NC 28307
1	ATTN: Library
	Director, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005
1	ATTN: SLCBR-TSB-S (STINFO)
	Commander, Dugway Proving Ground, Dugway, UT 84022
1	ATTN: Technical Library, Technical Information Division
	Commander, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783
1	ATTN: Technical Information Office
	Director, Benet Weapons Laboratory, LCWSL, USA AMCCOM, Watervliet, NY 12189
1	ATTN: AMSMC-LCB-TL
1	AMSMC-LCB-R
1	AMSMC-LCB-RM
1	AMSMC-LCB-RP
	Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E., Charlottesville, VA 22901-5396
3	ATTN: AIFRTC, Applied Technologies Branch, Gerald Schlesinger
1	Plastics Technical Evaluation Center, (PLASTEC), ARDEC, Bldg. 355N, Picatinny Arsenal, NJ 07806-5000
	Commander, U.S. Army Aeromedical Research Unit, P.O. Box 577, Fort Rucker, AL 36360
1	ATTN: Technical Library

No. of Copies	To
	Commander, U.S. Army Aviation Systems Command, Aviation Research and Technology Activity, Aviation Applied Technology Directorate, Fort Eustis, VA 23604-5577
1	ATTN: SAVDL-E-MOS
	U.S. Army Aviation Training Library, Fort Rucker, AL 36360
1	ATTN: Building 5906-5907
	Commander, U.S. Army Agency for Aviation Safety, Fort Rucker, AL 36362
1	ATTN: Technical Library
	Commander, USACDC Air Defense Agency, Fort Bliss, TX 79916
1	ATTN: Technical Library
1	Clarke Engineer School Library, 3202 Nebraska Ave. North, Ft. Leonard Wood, MO 65473-5000
	Commander, U.S. Army Engineer Waterways Experiment Station, P. O. Box 631, Vicksburg, MS 39180
1	ATTN: Research Center Library
	Commandant, U.S. Army Quartermaster School, Fort Lee, VA 23801
1	ATTN: Quartermaster School Library
	Naval Research Laboratory, Washington, DC 20375
1	ATTN: Code 5830
1	Dr. G. R. Yoder - Code 6384
	Chief of Naval Research, Arlington, VA 22217
1	ATTN: Code 471
1	Edward J. Morrissey, WRDC/MLTE, Wright-Patterson Air Force, Base, OH 45433-6523
	Commander, U.S. Air Force Wright Research & Development Center, Wright-Patterson Air Force Base, OH 45433-6523
1	ATTN: WRDC/MLLP, M. Forney, Jr.
1	WRDC/MLBC, Mr. Stanley Schulman
	NASA - Marshall Space Flight Center, MSFC, AL 35812
1	ATTN: Mr. Paul Schuerer/EH01
	U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899
1	ATTN: Stephen M. Hsu, Chief, Ceramics Division, Institute for Materials Science and Engineering
1	Committee on Marine Structures, Marine Board, National Research Council, 2101 Constitution Ave., N.W., Washington, DC 20418
1	Librarian, Materials Sciences Corporation, 930 Harvest Drive, Suite 300, Blue Bell, PA 19422
1	The Charles Stark Draper Laboratory, 68 Albany Street, Cambridge, MA 02139
	Wyman-Gordon Company, Worcester, MA 01601
1	ATTN: Technical Library
	General Dynamics, Convair Aerospace Division, P.O. Box 748, Fort Worth, TX 76101
1	ATTN: Mfg. Engineering Technical Library
1	Department of the Army, Aerostructures Directorate, MS-266, U.S. Army Aviation R&T Activity - AVSCOM, Langley Research Center, Hampton, VA 23665-5225
1	NASA - Langley Research Center, Hampton, VA 23665-5225
1	U.S. Army Propulsion Directorate, NASA Lewis Research Center, 2100 Brookpark Road, Cleveland, OH 44135-3191
1	NASA - Lewis Research Center, 2100 Brookpark Road, Cleveland, OH 44135-3191
	Director, U.S. Army Materials Technology Laboratory, Watertown, MA 02172-0001
2	ATTN: SLCMT-TML
1	Author

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
SITE COMPETITION OF IMPURITIES AND GRAIN BOUNDARY STABILITY IN IRON -
Genrich L. Krasko

Technical Report MTL TR 92-38, June 1992, 10 pp-illus

AD________________
UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words
Site competition
Grain boundaries
Iron

Impurities such as H, P, S, B, etc., have a very low solubility in iron and, therefore, prefer to segregate at the grain boundaries (GBs). In order to analyze the energetics of impurities on the iron GB, the Linear Muffin Tin Orbitals (LMTO) calculations were performed on a simple 8-atom supercell emulating a typical (capped trigonal prism) GB environment. The so-called *environment-sensitive* embedding energies (EE) were calculated for H, B, C, N, O, Al, Si, P, and S as a function of the electron charge density due to the host atoms at the impurity site. It was shown that, at the electron charge density typical of a GB, B and C have the lowest energy among the analyzed impurities and, thus, would compete with them for the site on the GB tending to push the other impurities off the GB. The above energies were then used in a modified Finnis-Sinclair embedded atom approach for calculating the equilibrium interplanar distances in the vicinity of a (111) $\Sigma 3$ tilt GB plane, both for the clean GB and that with an impurity. These distances were found to be oscillating, returning to the equilibrium spacing between (111) planes in bulk BCC iron by the 10th to 12th plane off the GB plane. H, B, C, N, and O actually dampen the deformation wave (making the oscillation amplitudes less than in the clean GB) while Al, Si, P, and S result in an increase of the oscillations. The effect of B, C, N, and O may be interpreted as cohesion enhancement; this conclusion supports our earlier first-principles results on B and C.

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
SITE COMPETITION OF IMPURITIES AND GRAIN BOUNDARY STABILITY IN IRON -
Genrich L. Krasko

Technical Report MTL TR 92-38, June 1992, 10 pp-illus

AD________________
UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words
Site competition
Grain boundaries
Iron

Impurities such as H, P, S, B, etc., have a very low solubility in iron and, therefore, prefer to segregate at the grain boundaries (GBs). In order to analyze the energetics of impurities on the iron GB, the Linear Muffin Tin Orbitals (LMTO) calculations were performed on a simple 8-atom supercell emulating a typical (capped trigonal prism) GB environment. The so-called *environment-sensitive* embedding energies (EE) were calculated for H, B, C, N, O, Al, Si, P, and S as a function of the electron charge density due to the host atoms at the impurity site. It was shown that, at the electron charge density typical of a GB, B and C have the lowest energy among the analyzed impurities and, thus, would compete with them for the site on the GB tending to push the other impurities off the GB. The above energies were then used in a modified Finnis-Sinclair embedded atom approach for calculating the equilibrium interplanar distances in the vicinity of a (111) $\Sigma 3$ tilt GB plane, both for the clean GB and that with an impurity. These distances were found to be oscillating, returning to the equilibrium spacing between (111) planes in bulk BCC iron by the 10th to 12th plane off the GB plane. H, B, C, N, and O actually dampen the deformation wave (making the oscillation amplitudes less than in the clean GB) while Al, Si, P, and S result in an increase of the oscillations. The effect of B, C, N, and O may be interpreted as cohesion enhancement; this conclusion supports our earlier first-principles results on B and C.

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
SITE COMPETITION OF IMPURITIES AND GRAIN BOUNDARY STABILITY IN IRON -
Genrich L. Krasko

Technical Report MTL TR 92-38, June 1992, 10 pp-illus

AD________________
UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words
Site competition
Grain boundaries
Iron

Impurities such as H, P, S, B, etc., have a very low solubility in iron and, therefore, prefer to segregate at the grain boundaries (GBs). In order to analyze the energetics of impurities on the iron GB, the Linear Muffin Tin Orbitals (LMTO) calculations were performed on a simple 8-atom supercell emulating a typical (capped trigonal prism) GB environment. The so-called *environment-sensitive* embedding energies (EE) were calculated for H, B, C, N, O, Al, Si, P, and S as a function of the electron charge density due to the host atoms at the impurity site. It was shown that, at the electron charge density typical of a GB, B and C have the lowest energy among the analyzed impurities and, thus, would compete with them for the site on the GB tending to push the other impurities off the GB. The above energies were then used in a modified Finnis-Sinclair embedded atom approach for calculating the equilibrium interplanar distances in the vicinity of a (111) $\Sigma 3$ tilt GB plane, both for the clean GB and that with an impurity. These distances were found to be oscillating, returning to the equilibrium spacing between (111) planes in bulk BCC iron by the 10th to 12th plane off the GB plane. H, B, C, N, and O actually dampen the deformation wave (making the oscillation amplitudes less than in the clean GB) while Al, Si, P, and S result in an increase of the oscillations. The effect of B, C, N, and O may be interpreted as cohesion enhancement; this conclusion supports our earlier first-principles results on B and C.

U.S. Army Materials Technology Laboratory
Watertown, Massachusetts 02172-0001
SITE COMPETITION OF IMPURITIES AND GRAIN BOUNDARY STABILITY IN IRON -
Genrich L. Krasko

Technical Report MTL TR 92-38, June 1992, 10 pp-illus

AD________________
UNCLASSIFIED
UNLIMITED DISTRIBUTION

Key Words
Site competition
Grain boundaries
Iron

Impurities such as H, P, S, B, etc., have a very low solubility in iron and, therefore, prefer to segregate at the grain boundaries (GBs). In order to analyze the energetics of impurities on the iron GB, the Linear Muffin Tin Orbitals (LMTO) calculations were performed on a simple 8-atom supercell emulating a typical (capped trigonal prism) GB environment. The so-called *environment-sensitive* embedding energies (EE) were calculated for H, B, C, N, O, Al, Si, P, and S as a function of the electron charge density due to the host atoms at the impurity site. It was shown that, at the electron charge density typical of a GB, B and C have the lowest energy among the analyzed impurities and, thus, would compete with them for the site on the GB tending to push the other impurities off the GB. The above energies were then used in a modified Finnis-Sinclair embedded atom approach for calculating the equilibrium interplanar distances in the vicinity of a (111) $\Sigma 3$ tilt GB plane, both for the clean GB and that with an impurity. These distances were found to be oscillating, returning to the equilibrium spacing between (111) planes in bulk BCC iron by the 10th to 12th plane off the GB plane. H, B, C, N, and O actually dampen the deformation wave (making the oscillation amplitudes less than in the clean GB) while Al, Si, P, and S result in an increase of the oscillations. The effect of B, C, N, and O may be interpreted as cohesion enhancement; this conclusion supports our earlier first-principles results on B and C.